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Preparation and electrochemical behavior of dopamine-selective polymeric membrane

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Summary

o-toluidine was polymerized electrochemically using constant-potential electrolysis at a gold electrode surface. Electrochemical behavior of dopamine and ascorbic acid at the polymer electrode prepared in this manner was examined by cyclic and differential pulse voltammetry techniques. The influence of chemical and electrochemical variables on dopamine selectivity of the polymer electrode was systematically investigated and the optimal values for each parameter were determined. Experimental results showed that optimized polymeric membrane exhibited selectivity for dopamine while blocking ascorbic acid. Therefore, it is claimed that poly (*o*-toluidine) film can be used as a dopamine-selective polymeric membrane in the presence of ascorbic acid.

Key Words: poly (*o*-toluidine); selective membrane; dopamine

Introduction

In recent years, electrochemically synthesized conducting or non-conducting polymeric coatings have became of increasing interest because of their wide range of applications such as gas sensors (1-3), biosensors (4-9) and permselective membranes (10, 11).

Dopamine is one of the electroactive species in brain extracellular fluid and its function is to regulate neural interactions by reducing permeability of gap junctions between adjacent neurons of the same type.

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Dopamine in central nervous systems coexists with ascorbic acid, whose redox potential is often similar to the potential of dopamine (12). Therefore, one of the most important problems when electrochemically measuring dopamine in a biological fluid is the presence of electroactive ascorbic acid, which reduces the sensitivity and selectivity of dopamine (13). This problem can be circumvented by using selective polymeric membranes, which enhance the selectivity of dopamine against ascorbic acid. Electrochemically or chemically prepared polymeric films have been used to distinguish between the oxidation peaks of dopamine and ascorbic acid. The response to ascorbic acid, being an anion at the physiological pH, is completely eliminated when a nafion coated glassy carbon is used, for nafion is an anionic polymer (14). The oxidation of ascorbic acid is electrocatalysed over polypyrrole due to electrostatic interaction between the fixed positive cites in the polymer and the ascorbate anion (15). However, overoxidized polypyrrole contains carbonyl and carboxylic groups that create a diffuse, high electron density in the film and that causes dopamine to be selectively oxidized (16).

In previous works, we have reported the electrochemical synthesis and optimization of poly (*o*-toluidine) film as the permselective membrane for hydrogen peroxide and as the immobilization media for glucose oxidase (17,18). It is believed that the electropolymerization mechanism of *o*-toluidine proceeds via a radical cation which reacts with a second radical cation to form a dimer. The resulting dimer reacts further with other monomer radical to produce the polymeric chain (19, 20). In the present article, we focus on one-step preparation, optimization and electrochemical properties of poly (*o*-toluidine) film as the dopamine- selective membrane.

Experimental

Materials

o-Toluidine (Merck, Darmstad) was purified by distillation using standard techniques before use. All other chemicals such as dopamine hydrochloride, ascorbic acid, NaCl, Na_2SO_4, $NaClO_4$ and KC1 were of analytical grade and purchased from E. Merck Darmstadt, Germany. All solutions were prepared with doubly-distilled water. Ascorbic acid and dopamine solutions were prepared freshly for each experiment.

Instrumentation

Electrochemical polymerization, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out with a BAS 100W (Bioanalytical Systems, Inc. West Lafeyette, IN, USA) electrochemical analyzer. All electrochemical experiments were conducted in a three-electrode cell by using a gold disc (geometric area: 1.98 mm^2) as working electrode and a Pt coil as an auxiliary electrode together with a Ag/AgCl reference electrode.

Preparation of polymer films and electrochemical measurements

Before each polymerization, Au electrodes to be used as the working electrode were polished with successively finer grades of diamond polishing compounds and aqueous alumina slurry (Johnson Matthey Catalog Comp., USA) down to 0.5 µm. Poly (*o*-toluidine) coatings were generated by potentiostatically electropolymerizing relevant monomer from nitrogen-saturated aqueous solution. Selectivity characteristics in aqueous solution containing dopamine and/or ascorbic acid of the resultant polymeric films were examined by voltammetric techniques such as CV and DPV. For this reason, a three-electrode cell consisting of the polymer-coated Au working electrode, a Pt wire counter electrode and a Ag/AgCl reference electrode was employed.

Results and discussion

Electrochemical Polymerization

Figure 1A and 1B represent the typical cyclic voltammograms of the bare gold electrodes in the absence and presence of the monomer, respectively.

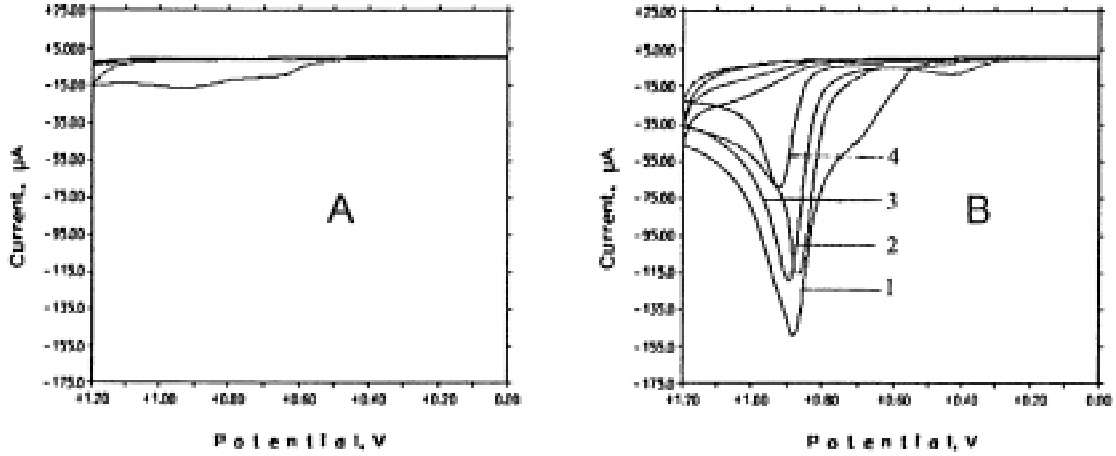

Figure 1. Cyclic voltammograms obtained with the bare gold electrode in 0.1M KCl (A) and 0.1M KCl + 0.1M *o*-toluidine (B), Scan rate = 50 mV/s.

From the comparison of the voltammograms, it is seen that monomer starts to oxidize at approx. 0.65 V and oxidation peak potentials shift slightly to higher values during the second and subsequent scans. As we previously reported for Pt substrates (18), this voltammetric behavior is typical for electrochemically generated electroactive polymers. Although it was observed in Figure 1 that *o*-toluidine can be polymerized electrochemically at the higher potential values, polymerization was carried out at 0.75 V so as to secure a controllable film growth at a slow electrolysis rate.

Optimization of poly (o-toluidine) film as a dopamine selective membrane

Poly (*o*-toluidine) film to be used as a permselective membrane must be selective to dopamine in the presence of ascorbic acid. Film thickness which can be expressed as the charged consumed and adequately controlled during the electropolymerization is one of the most effective factors to be considered in improving of the permselectivity character of the resulting polymeric film. Polymeric films at desired thicknesses (corresponding to 6-11 mC of charge passage) were prepared in order to determine the optimal film thickness which prevent ascorbic acid permeation while allowing dopamine through film. From DPV data, it was seen that peak currents for dopamine increased with increasing film thickness and reached to a maximum value at ca. 8 mC, after which it decreased. Thus, optimal film thickness of the polymer electrode was chosen as 8 mC. In the similar manner, the effect of the monomer concentration in the polymerization solution was studied in the range of 50 - 250 mM and optimal monomer concentration was found as 0.1M. Then, effect of the electrolyte type used in DPV measurements was examined for Na_2SO_4, KCl, $NaNO_3$, NaCl and $NaClO_4$ electrolytes and the highest peak current for dopamine was obtained for Na_2SO_4. In brief, the experimental conditions were as follows: applied potential; 0.75 V vs Ag/AgCl, polymeric film thickness; 8 mC, monomer concentration; 0.1 M and electrolyte; Na_2SO_4.

Voltammetric behavior of ascorbic acid and dopamine at the polymer electrode

Figure 2 compares cyclic voltammetric behaviors of ascorbic acid, dopamine and ascorbic acid plus dopamine mixture at the bare gold and optimized poly (*o*-toluidine) modified electrodes. As can be seen, when compared with the bare gold electrode, the voltammogram of ascorbic acid at the polymer electrode shows no oxidation peak (Fig. 2B).

This behavior means that the poly (*o*-toluidine) film suppresses ascorbic acid oxidation. On the other hand, polymer electrode in the presence of dopamine shows an oxidation peak at ca. 0.50 V (Fig. 2D). Moreover, the voltammogram obtained at the polymer electrode for dopamine is similar to that of dopamine plus ascorbic acid mixture (Fig. 2F). From these findings, it is concluded that optimized polymeric film prevents oxidation of ascorbic acid, but permit dopamine oxidation. In other words, optimized poly (*o*-toluidine) film electrode might be suitable for the selective determination of dopamine in the presence of ascorbic acid.

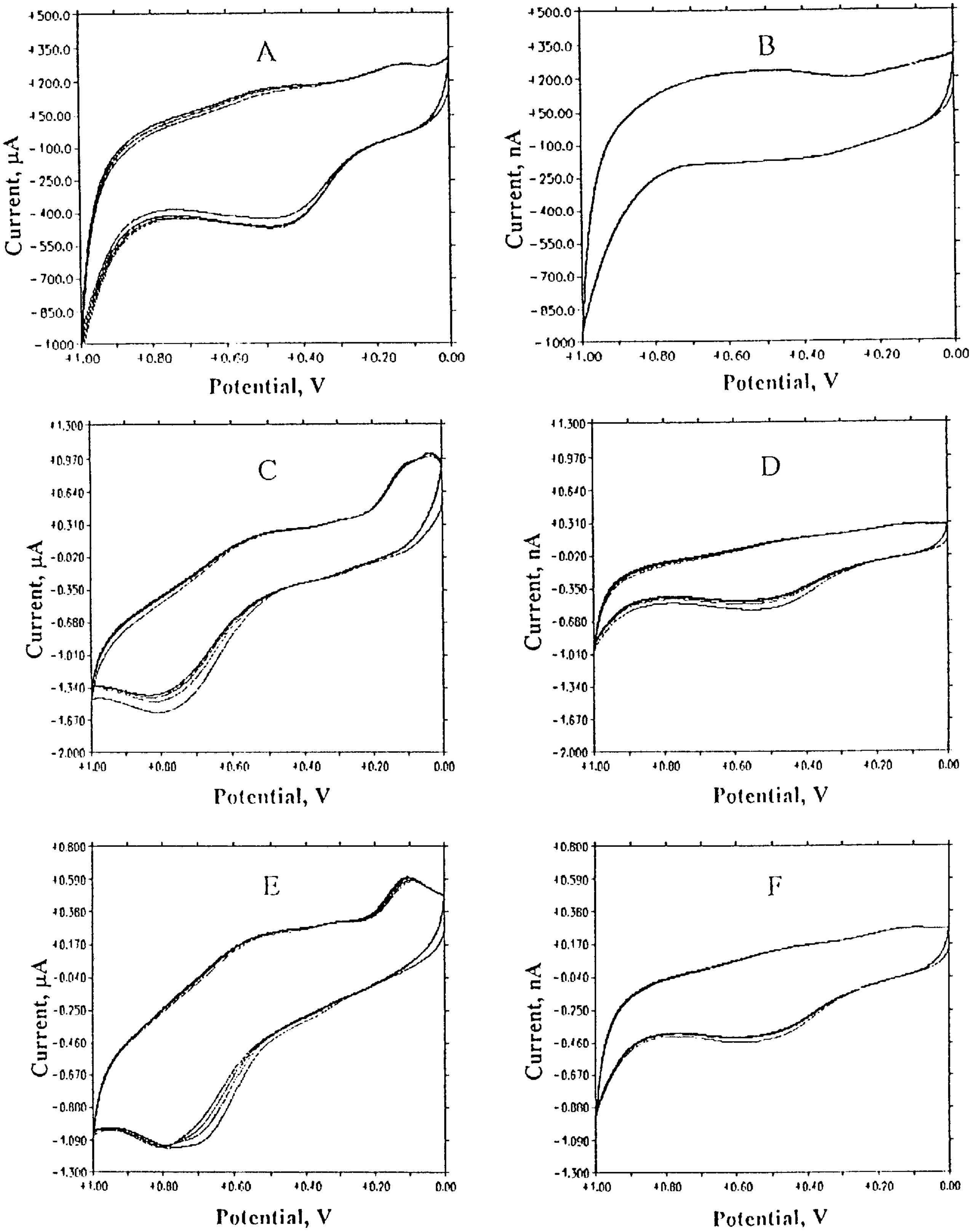

Figure 2. CVs of ascorbic acid (A,B), dopamine (C,D) and ascorbic acid plus dopamine mixture (E,F) at the bare gold (A,C,E) and optimized polymer electrode (B,D,F). Concentrations of the species: [dopamine] = [ascorbic acid] = 10 mM, Scan rate = 50 mV/s, Electrolyte:Na_2SO_4 (pH 6.0).

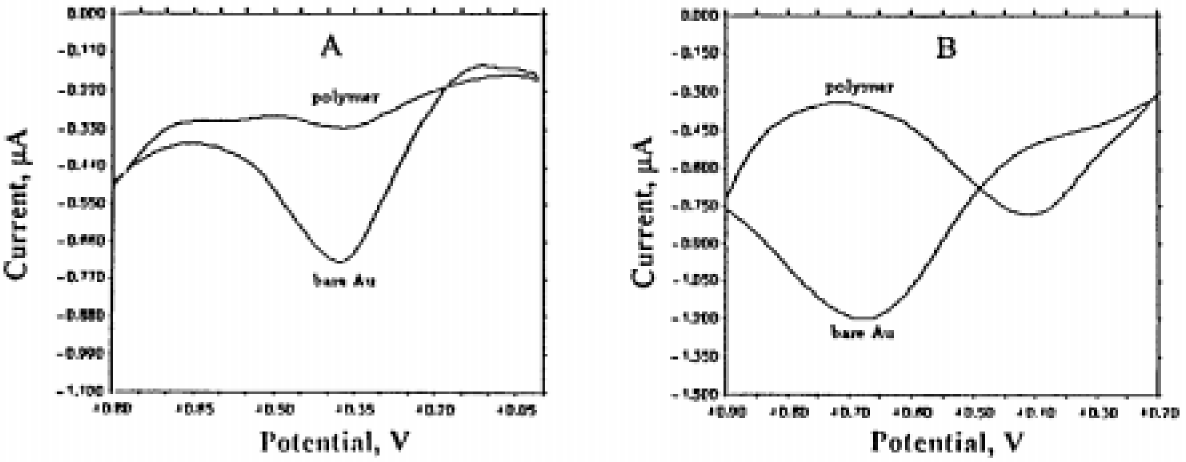

Figure 3. DPV of 10 mM ascorbic acid (A) and 10 mM dopamine (B) at the bare Au and optimized polymer electrodes. Scan rate = 50 mV/s, Electrolyte:Na_2SO_4 (pH 6.0).

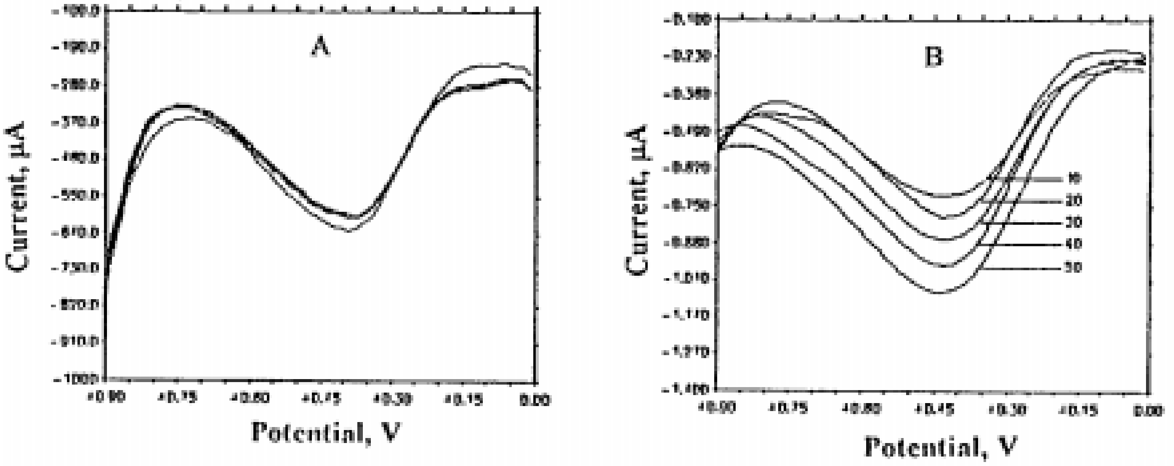

Figure 4. DPV of 10 mM dopamine at various concentrations of ascorbic acid (10-50 mM) (A), DPV of 10 mM ascorbic acid at various concentrations of dopamine (10-50 mM) (B) at optimized polymer electrode. Scan rate = 50 mV/s, Electrolyte:Na_2SO_4 (pH 6.0).

Differential pulse voltammograms of ascorbic acid and dopamine at the bare gold and optimized poly (*o*-toluidine) electrodes are shown in Figure 3. As expected and observed on the DPVs, optimized polymer electrode is selective for dopamine while rejecting ascorbic acid passage through the film. Also, as depicted in Figure 4, it is easily seen that dopamine peak was unaffected with the varying ascorbic acid concentrations (A) and, that peak heights increased with an increase in concentrations of dopamine in the presence of ascorbic acid (B). The responses for dopamine were also linear between 5 and 40 µM, although of a lesser magnitude (nA). Moreover, the voltammograms obtained with the polymer electrode in dopamine plus ascorbic acid mixture showed that its response was almost invariable for the successive runs. This means that polymer stability was satisfactory.

In brief, it was demonstrated in the present study that dopamine-selective poly (*o*-toluidine) film could be easily prepared by electrochemical polymerization of the corresponding monomer in an aqueous solution on Au electrode surface. Dopamine selectivity in the presence of ascorbic acid of the polymeric membrane prepared in this one-step procedure was investigated by electrochemical techniques such as CV and DPV. From voltammetric data, we have demonstrated that poly (*o*-toluidine) film can be used as a dopamine-selective polymeric membrane in the presence of ascorbic acid.

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